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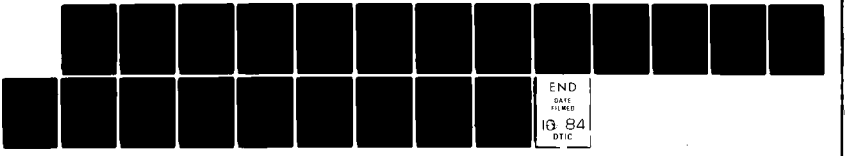

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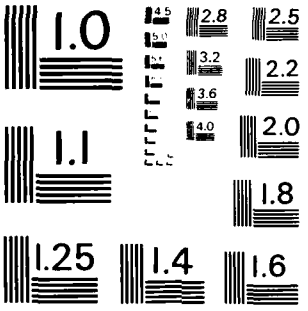

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$-\Delta G_f^o/R$ (kilokelvins), are: 1/3 VSi_2, 4.25; 1/11 V_6Si_5, 5.25; 1/8 V_5Si_3, 5.47; 1/4 V_3Si, 4.40. These data, when combined with heat capacity and entropy data from the literature, give standard enthalpies of formation at 298.15K, $-\Delta H_f^o/R$ (kilokelvins): 1/3 VSi_2, 4.90; 1/11 V_6Si_5, 5.93; 1/8 V_5Si_3, 6.31; 1/4 V_3Si, 5.40.

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TECHNICAL REPORT NO. 2

THERMODYNAMICS AND PHASE EQUILIBIRA IN THE VANDIUM-SILICON SYSTEM

by

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THERMODYNAMICS AND PHASE EQUILIBRIA IN THE VANDIUM-SILICON SYSTEM

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ABSTRACT

The vandium-silicon system has been investigated by Knudsen cell-mass spectrometry in the temperature range 1600-2000K. Thermodynamic activities were obtained by direct comparison with the elements. Vanadium silicide was shown to have a negligible range of homogeneity and V_6Si_5 to be stable only at high temperatures. Standard free energies of formation at 1650K, $-\Delta G_f^o/R$ (kilokelvins), are: 1/3 VSi_2, 4.25; 1/11 V_6Si_5, 5.25; 1/8 V_5Si_3, 5.47; 1/4 V_3Si, 4.40. These data, when combined with heat capacity and entropy data from the literature, give standard enthalpies of formation at 298.15K, $-\Delta H_f^o/R$ (kilokelvins): 1/3 VSi_2, 4.90; 1/11 V_6Si_5, 5.93; 1/8 V_5Si_3, 6.31; 1/4 V_3Si, 5.40.

Index entries: effusion, mass spectrometry, vanadium silicides, pnase equilibria, range of homogeneity, thermodynamics, activities, free energies of formation, enthalpies of formation.

INTRODUCTION

There has been interest in the transition metal silicides for several decades because of their refractory properties, hardness, and corrosion resistance. More recently, these materials are being applied as gate electrodes and conductors in very large scale integration (VLSI) devices. In addition, a systematic study of stability trends in a series of transition metal silicides and related compounds, of which this is part, may give insight into factors affecting the strengths of chemical bonds in solids.

Several reviews of the vanadium-silicon system have appeared in the literature.[1-5] Although VSi_2, V_5Si_3, and V_3Si are well established, there are several matters on which there is less agreement. For example, Hansen[1] shows a wide range of homogeneity for VSi_2, but Smith[5] reports a negligible range. Conversely, Hansen's phase diagram presents V_3Si as a "line" compound, whereas Smith's shows a range of homogeneity. In addition, Smith's diagram, Fig. 1, includes V_6Si_5, but Hansen's does not. Chart,[6,7] Freund and Spear,[8] and Smith[5] have critically reviewed published thermochemical data for the vanadium-silicon system. These data were obtained by combustion calorimetry,[9] direct reaction calorimetry,[10,11] and EMF measurements.[12,13,14] Consideration of both binary[6,7] and ternary[8] phase diagrams were included in the assessments cited. The EMF data appear to be most reliable. The heat capacity and entropy data needed to compare results obtained at different temperatures were also reviewed,[5-8] and missing data were estimated.[5] There is a need to determine whether V_6Si_5 is a stable compound and, if so, the temperature range of its stability. In addition, in view of the heavy reliance on the EMF data[12-14] in the critical assessments,[5-8] an independent determination of vanadium silicide stabilities is desirable. The use of mass spectrometry combined with Knudsen effusion, as described below, permits

direct determination of thermodynamic activity at high temperatures as a function of composition, hence giving boundaries of phase regions, together with partial and integral free energies. The range of temperatures available is of comparable breadth to that of the earlier EMF measurements,[12-14] but it is some 500K or more higher in temperature.

EXPERIMENTAL METHOD

Samples were prepared by arc-melting the mechanically mixed elements under purified argon. The V metal contained the following detected elements: Cu(200 ppm), Fe(90 ppm) and Cr(270 ppm). Crystal bar Si of 99.99% purity was used. They were subsequently annealed for several hours under vacuum at temperatures approaching the appropriate eutectic or melting temperature. Residues from the experiments were characterized by x-ray Debye-Scherrer powder diffraction and wet chemical analysis for vanadium.

The apparatus used in this study has been described in part in earlier[15-18] papers and consists of a 60^{0} sector single focusing mass spectrometer combined with a Knudsen effusion cell. While this instrument is similar to the design pioneered by Chupka and Inghram,[19] it has a number of unique features which make it particularly well-suited for the direct determination of thermodynamic activities at high temperatures. A rapid turn-around between samples permits a direct comparison, within a 3-4 hour period during which instrument sensitivity is constant, of the ion currents from a sample and from a pure element, both as a function of temperature. The vacuum system is designed to accomplish this facility in changing samples. The furnace section of the instrument is evacuated by a mercury diffusion pump and the source and analyzer sections by ion pumps. Since mercury does not react with nitrogen at pump operating temperatures, it is not necessary to cool or isolate the pump before venting the system with pure nitrogen. Once a sample has cooled, a new sample may be placed in the instrument and evacuation begun in a matter of minutes.

The only portion of the apparatus exposed to air is the effusion cell assembly, its support, and the radiation shields immediately below it. Since pure nitrogen flows through the apparatus continuously when it is at atmospheric pressure, the rest of the apparatus is not exposed to air. Hence, pump-down is rapid and measurements may be resumed with a new sample within 15-20 minutes. In addition to these features of the vacuum system, the source is designed to maximize sensitivity to the greatest extent possible,[18] which allows operation at sufficiently low temperatures so that changes in sample composition during an experiment are minimal to negligible. Temperatures are measured with a photon counting pyrometer[16,17] which permits temperatures from 1400K to 2200K to be measured routinely to within 0.5K and 1.0K, respectively, of IPTS-68. The Knudsen cell assembly and electron bombardment heating system are designed[20] to minimize temperature gradients and their effects on the reliability of experimental results. Samples were contained in a tungsten cup within the effusion cell assembly having a tantalum carbide lid. The samples reacted with tungsten but not with TaC. Silicon signals were obtained at an electron energy of 12.3V in order to minimize interference from the background peak at mass 28; vanadium signals were measured at electron energies of 20.8 V.

EXPERIMENTAL RESULTS AND DISCUSSION

Data are fitted to the equation

$$\log IT = A/T + B \qquad (1)$$

by the method of least squares. For the pure elements the parameter B is calculated in accord with a fixed A value of -26278 for V and -23733 for Si. The activity of each element is given by

$$\log a_i = (A_i - A_i^0)/T + (B_i - B_i^0) \qquad (2)$$

where A_i^0 and B_i^0 refer to the pure element.

The vertical lines in Fig. 1 give the compositions and temperature ranges covered in this study. A typical day's activities involved measuring pure silicon, a change to the silicide sample, measuring the silicon and vanadium signals, a change to a pure vanadium sample, and finally measuring pure vanadium. Data for one such day are shown in Fig. 2. Figure 3 gives a plot of log a_i *vs* X_{Si} at 1650K. The activities at a given composition were used to calculate the Gibbs energy of phase formation:

$$(1-X)V_{(s)} + XSi_{(s)} = V_{1-X}Si_{X(s)} \qquad (3)$$

$$\Delta G_f^o /R = 2.303\ T \log a_V^{(1-X)} a_{Si}^X \qquad (4)$$

where X is the atom fraction of Si. For samples more vanadium-rich than V_6Si_5, log a_{Si} in each subsequent two-phase region was calculated from log a_V and $\Delta G_f^o/R$ of the previous compound. A Gibbs-Duhem comparison between a_{Si} and a_V was not possible because the two activities were not measured in the same single phase region. Entropy and heat capacity data for the silicides cited or estimated by Smith[5] were used with Smith's[21] data for vanadium and data from the JANAF Tables[22] for silicon, together with the experimental results, to calculate both $\Delta G_f^o/R$ as a function of temperature as shown in Fig. 4. and the free energy and enthalpy data given in Table 1. For comparison, these presentations also include stability data[5] based on the EMF studies.[12-14] Agreement is rather good except for V_3Si. The results of this study generally support the phase diagram presented by Smith.[5] Each phase will be discussed individually as follows:

$\underline{VSi_2}$

The homogeneity range of VSi_2 is negligible. This was demonstrated in one run with a VSi_2 sample for which the pyrometer sight hole was quite large owing to a damaged cell, so that there was some evolution of sample

composition and silicon activity as the run progressed. The data for this run are presented in Fig. 3 as the points labeled "x". The total loss in mass of the 600 mg sample was calculated from the effusion equation to be 2 mg or less, which corresponds to a change in the Si/V ratio of less than 0.01. When the sample was returned to an undamaged cell, after this composition change, no further change in Si activity was observed. This indicates that the concentration gradient within the sample must have been negligible.

V_6Si_5

The lower temperature limit of stability of V_6Si_5 may be estimated by simultaneous solution of the equations:

$$\log a_i = (A_i - A_i^o)/T + (B_i - B_i^o) \qquad (2a)$$

$$\log a_j = (A_j - A_j^o)/T + (B_j - B_j^o) \qquad (2b)$$

where a_i and a_j represent activities of an element in the VSi_2-V_6Si_5 and V_6Si_5-V_5Si_3 two-phase regions, respectively, since a_i and a_j become equal at the temperature of disproportionation of V_6Si_5 into VSi_2 and V_5Si_3. That temperature was found to be 1160 $\pm$ 100K.

V_3Si

This study supports a range of homogeneity for V_3Si, extending to X_{Si} = 0.21 or lower at 1800K. An enlarged view of $\log a_V$ vs X_{Si} at 1300K for the composition range near V_3Si is shown in Fig. 5. While this plot shows clear evidence for extended homogeneity of V_3Si, the data do not permit a precise location of the lower boundry of the single phase region. Additional evidence for extended homogeneity is available in the plot of precision lattice constants for cubic V_3Si as a function of composition which is given in Fig. 6. These values were obtained by a standard extrapolation procedure[23] from x-ray powder diffraction data of effusion residues. The plot includes data given by Bruning[24] for

samples annealed at 1273K. The results of the present study are in agreement with those of Bruning[24] but not with those of Efimov[25] or Seeber and Nickl[26] who found the homogeneity range of V_3Si to be 1 atomic percent Si or less up to 1773K. Since all measurements except the activity measurements of the present study were made at room temperature, albeit on quenched samples in one study,[25] they can be largely discounted. Our evidence supports extended homogeneity for V_3Si at high temperatures.

ACKNOWLEDGEMENTS

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TABLE I

STABILITY DATA FOR VANADIUM SILICIDES

	$-\Delta G^{o}_{f,1650}/R$	$-\Delta H^{o}_{f,298}/R$	$-\Delta H^{o}_{f,298}/R$ *
	(kilokelvins)	(kilokelvins)	(kilokelvins)
1/3 $VSi_{2(s)}$	4.25 ± 0.02	4.90 ± 0.02	4.90 ± 0.10
1/11 $V_6Si_{5(s)}$	5.25 ± 0.02	5.93 ± 0.04	5.97 ± 0.3
1/8 $V_5Si_{3(s)}$	5.47 ± 0.05	6.31 ± 0.06	6.47 ± 0.2
1/4 $V_3Si(s)$	4.40 ± 0.05	5.40 ± 0.05	5.18 ± 0.2

* Ref. 5

LIST OF FIGURES

1. V-Si System, after Smith[5]

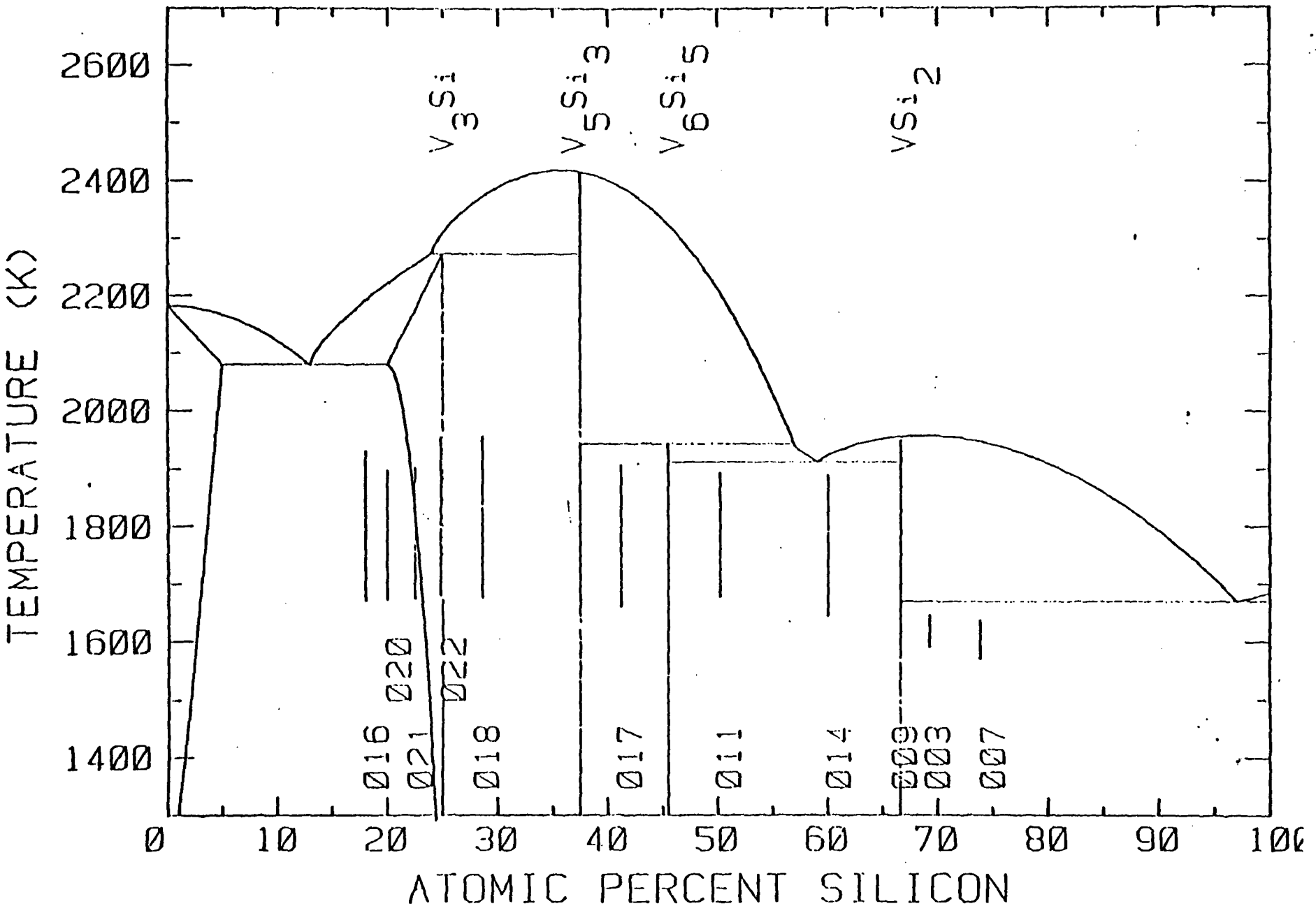
2. Typical Results for One Day

3. Log a vs X_i at 1650K

4. $\Delta G_f/R$ vs T

5. Log a_V vs X_{Si} Near V_3Si

6. Lattice Parameters of V_3Si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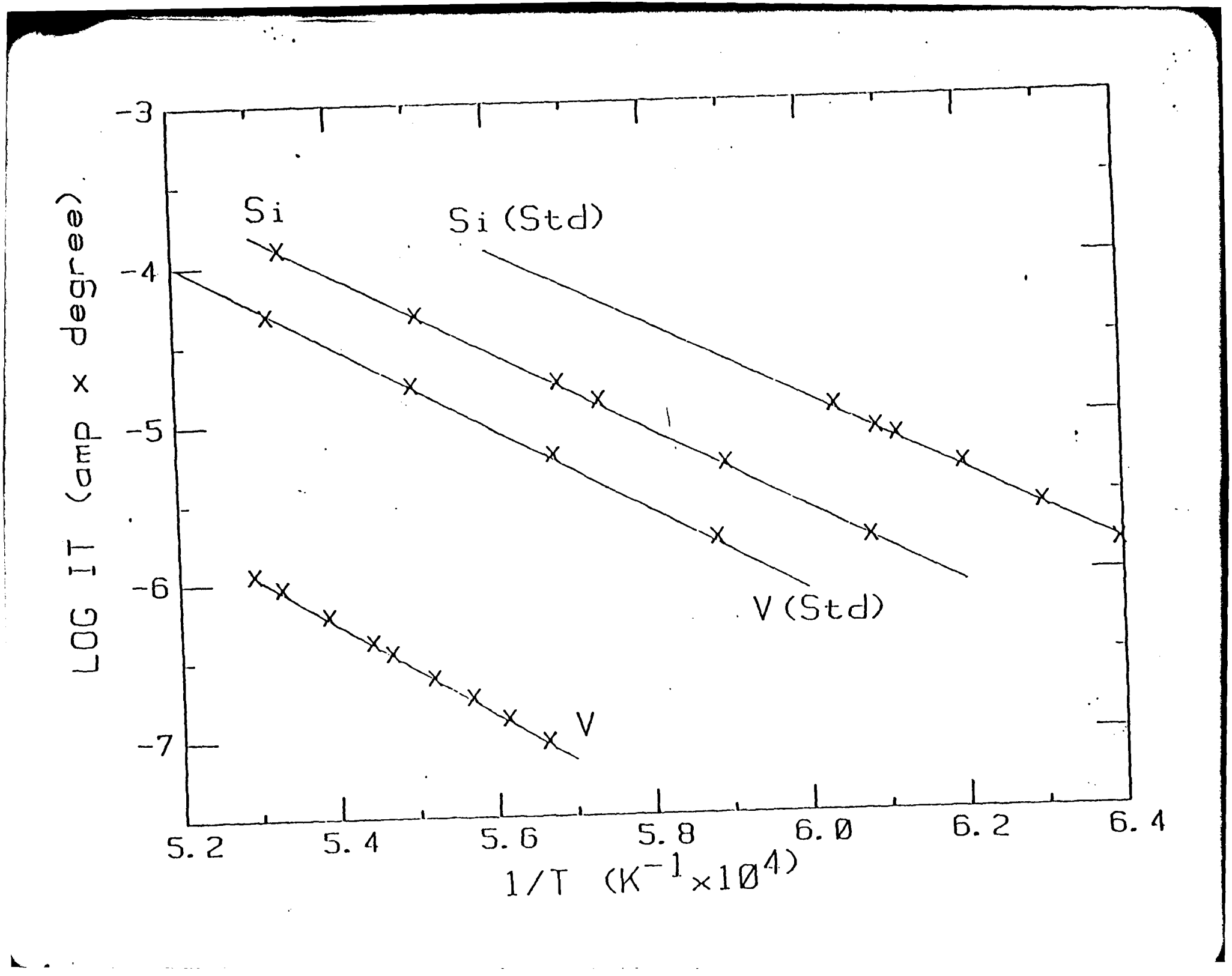
2400
2200
2000
1800
1600
1400
0
10
20
30
40
50
60
70
80
90
100
ATOMIC PERCENT SILICON
V3Si
V5Si3
V6Si5
VSi2
016
020
021
022
018
017
011
014
009
003
007


Si
Si (Std)
V (Std)
V
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-4
-5
-6
-7
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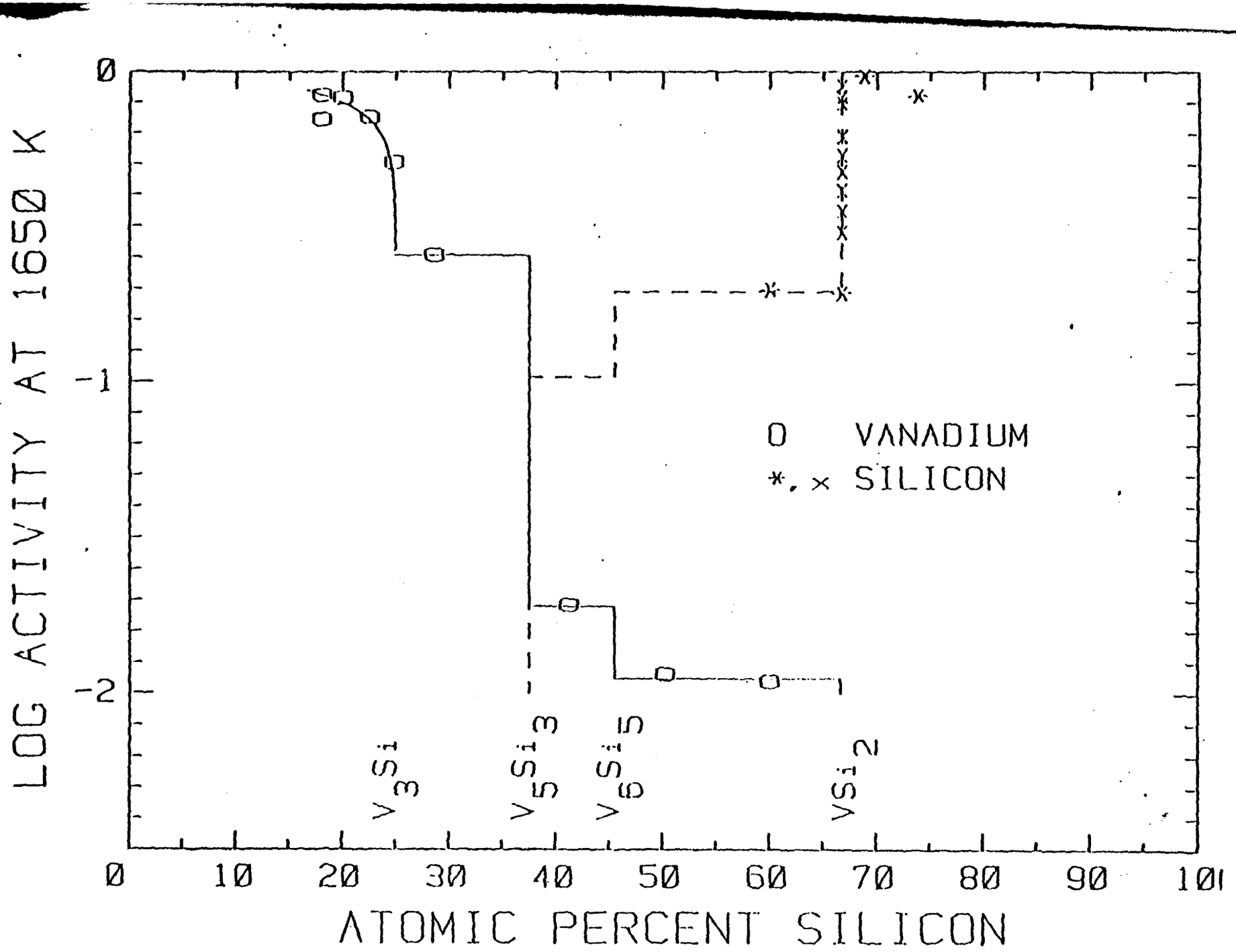
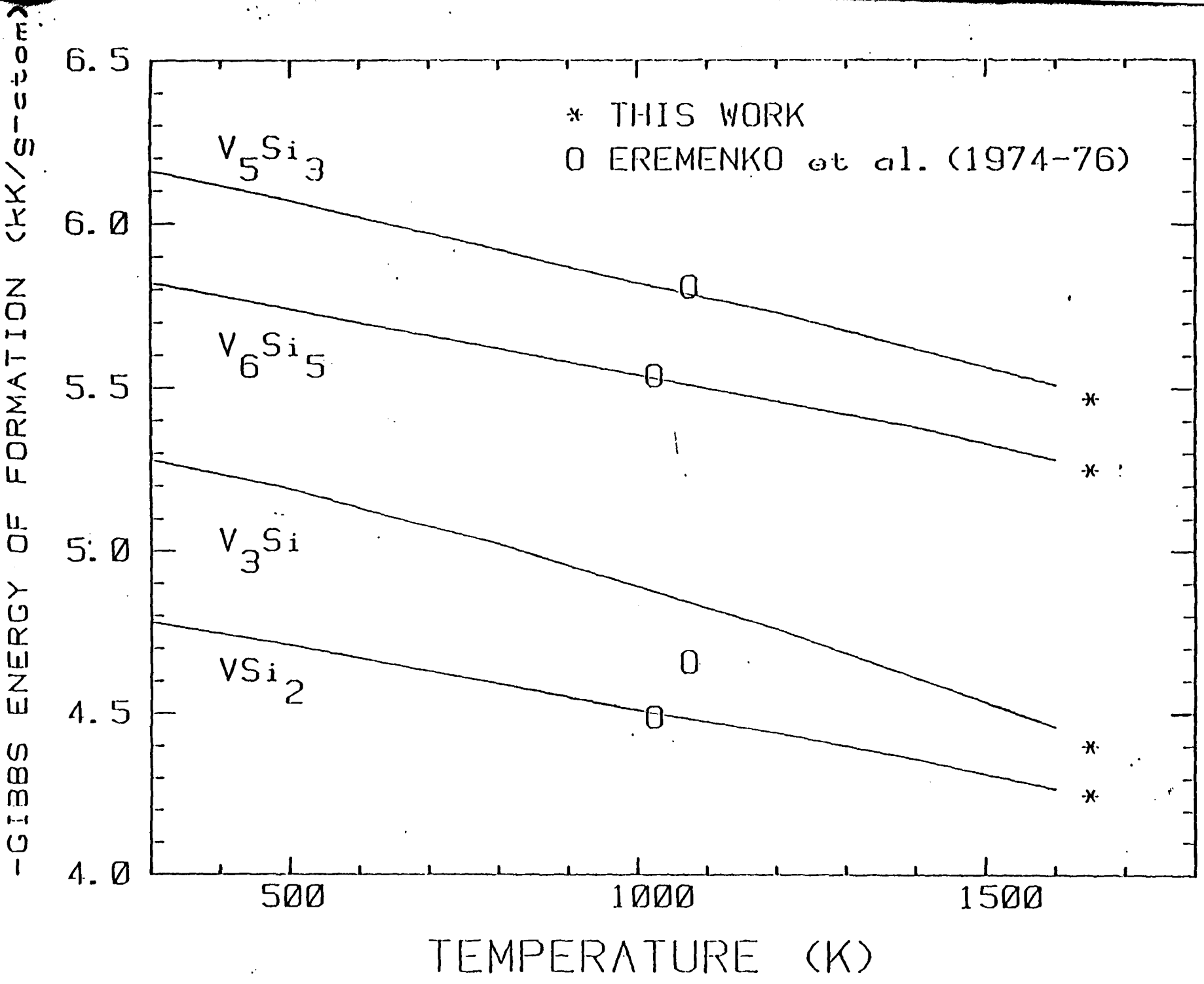
5.4
5.6
5.8
6.0
6.2
6.4
1/T (K⁻¹ x 10⁴)


LOG ACTIVITY AT 1650 K
0
-1
-2
0 VANADIUM
*, × SILICON
V3Si
V5Si3
V6Si5
VSi2
0
10
20
30
40
50
60
70
80
90
100
ATOMIC PERCENT SILICON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6.0
5.5
5.0
4.5
4.0
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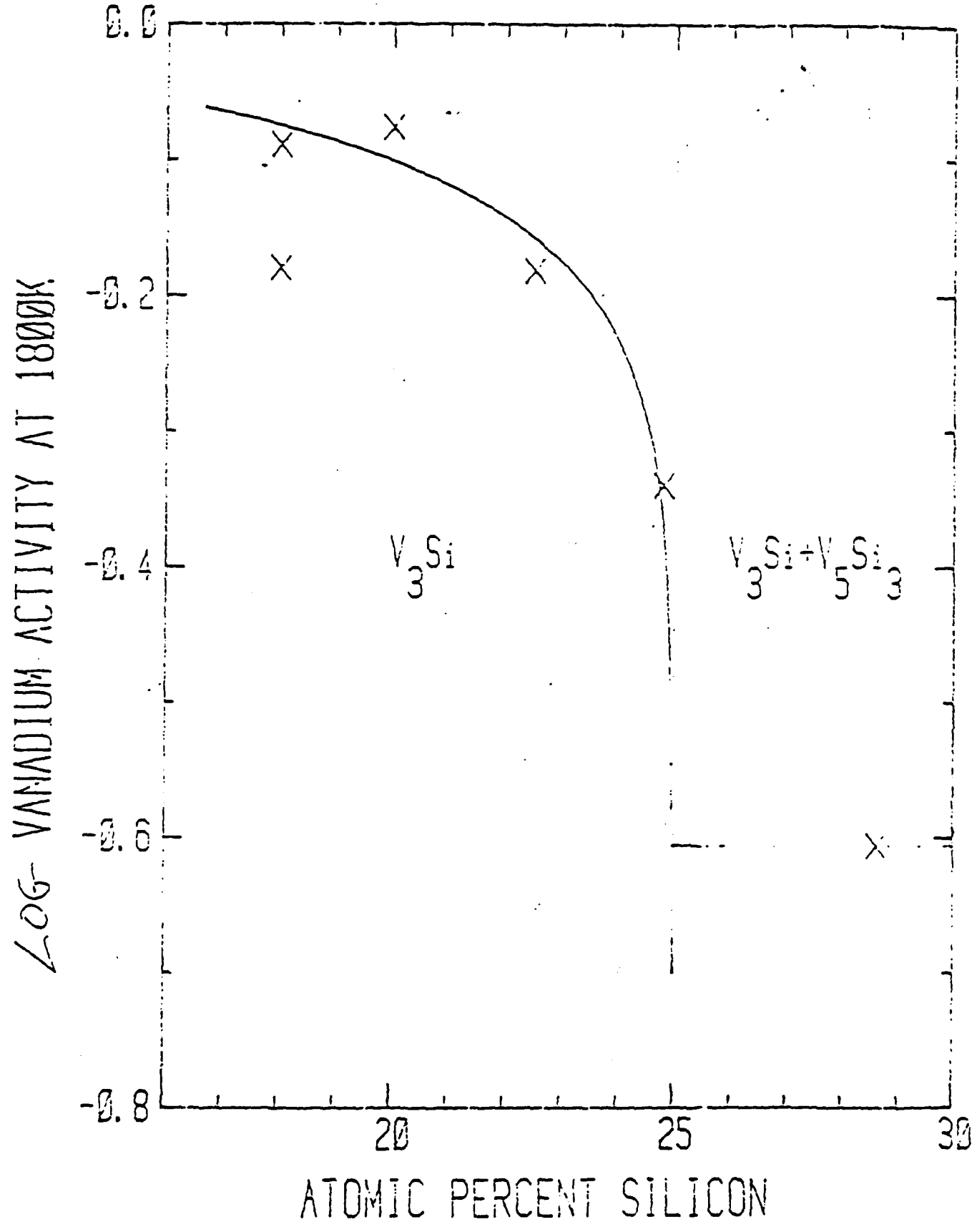
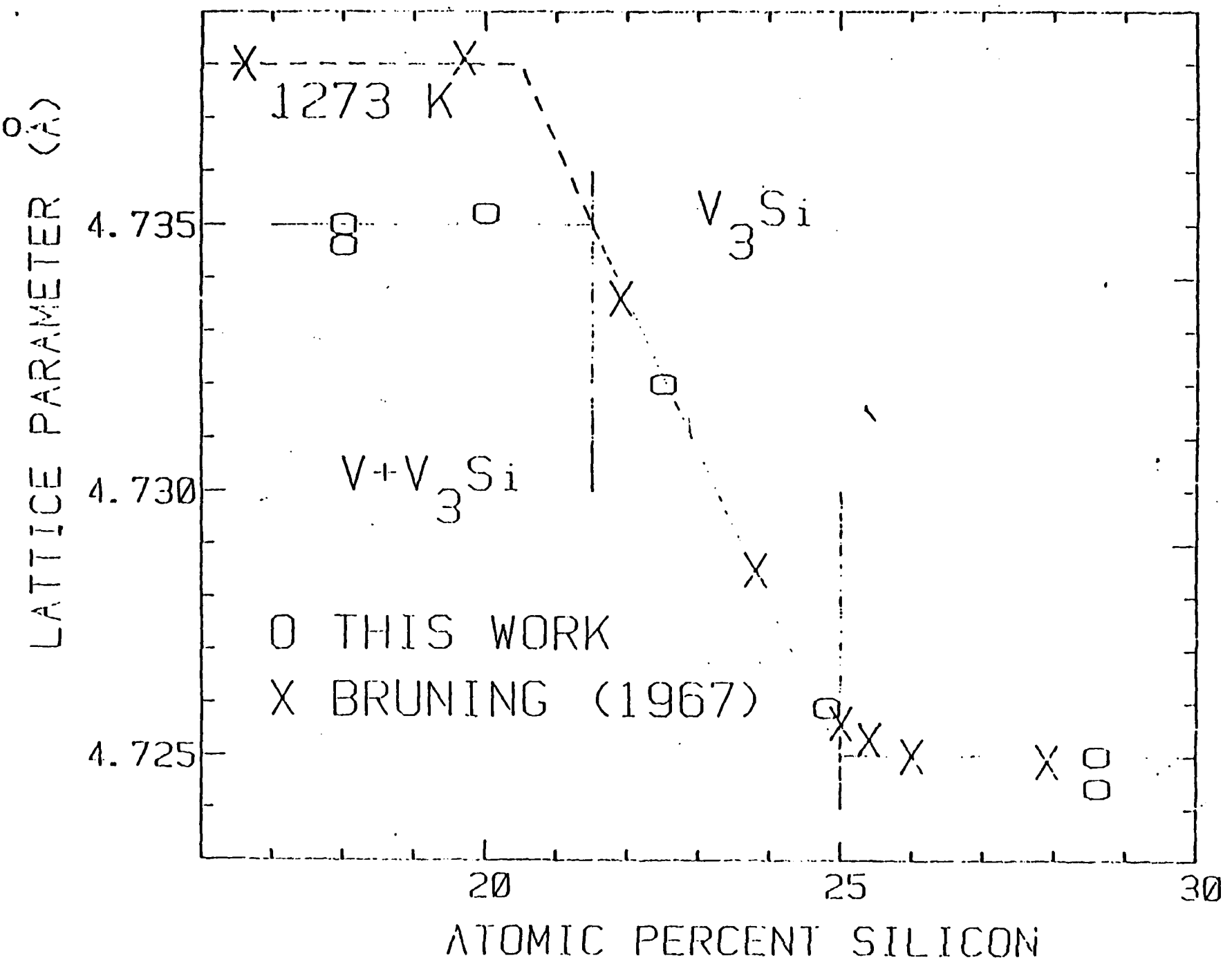
1000
1500
TEMPERATURE (K)
* THIS WORK
O EREMENKO et al. (1974-76)
V5Si3
V6Si5
V3Si
VSi2


0.0
-0.2
-0.4
-0.6
-0.8
LOG VANADIUM ACTIVITY AT 1800K
V_3Si
$V_3Si+V_5Si_3$
20
25
30
ATOMIC PERCENT SILICON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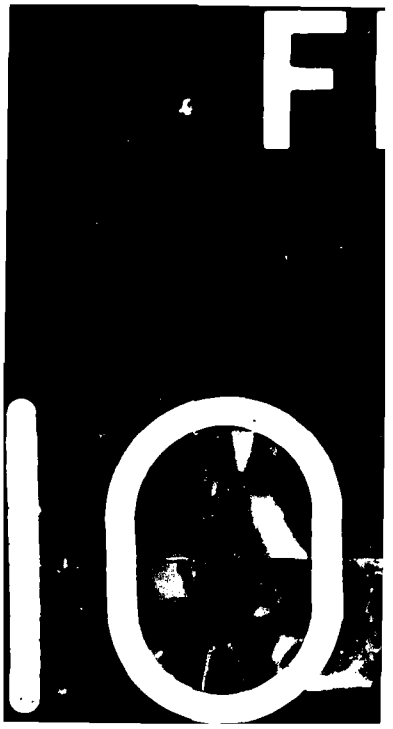
4.730
4.725
1273 K
V3Si
V+V3Si
O THIS WORK
X BRUNING (1967)
20
25
30
ATOMIC PERCENT SILICON


F
IQ